other industrial waters, and strong alkali solutions. It is possible to automate fully the preconcentration and separation/analysis procedure. In an example of this trace levels of Mg^{2+}, Ca^{2+} and transition metals in biological and environmental samples are preconcentrated on two iminodiacetic acid-type chelating ion exchanger and one strong acid cation exchanger connected in series. The preconcentrated metal ions are then removed from the three columns and the concentrated metal ion mixture is separated on an analytical Ion Pac CS5 column by an elution programme that takes into account pH, ammonia/ammonium ion buffer concentration and PDCA concentration. Detection is by absorption after postcolumn reaction of the metal ions with PAR.

See also: **II/Chromatography: Liquid:** Mechanisms: Ion Chromatography. **Extraction:** Analytical Inorganic Extractions. **Ion Exchange:** Theory of Ion Exchange. **III/Ion Analysis:** Liquid Chromatography.

Further Reading

Barkley DJ, Blanchette M, Cassidy RM and Elchuk S (1986) Dynamic chromatographic systems for the determination of rare earths and thorium in samples from uranium ore refining processes. *Analytical Chemistry* 58: 2222–2226.

Cagniant D (1992) *Complexation Chromatography*. New York: Dekker.

Elchuk S and Cassidy RM (1979) Separation of the lanthanides on high-efficiency bonded phases and conventional ion-exchange resins. *Analytical Chemistry* 5: 1434–1438.

Haddad PR and Jackson PE (1990) *Ion Chromatography Principles and Applications*, p. 232. Amsterdam: Elsevier.

Hilton DF and Haddad PR (1986) Determination of metal-cyano complexes by reversed phase ion-interaction high performance liquid chromatography and its application to the analysis of precious metals in gold processing solutions. *Journal of Chromatography* 361: 141–150.

Inczédy J (1966) *Analytical Applications of Ion Exchangers*. Oxford: Pergamon Press.

Kraus KA and Moore GE (1953) Anion exchange studies. VI. The divalent transition elements manganese to zinc in hydrochloric acid. *Journal of the American Chemical Society* 74: 1460–1462.

Pietrzyk DJ (1989) Macroporous polymers. In Brown PR and Hartwick RA (eds) *High Performance Liquid Chromatography*, p. 244, New York: Wiley-Interscience.

Siriraks A, Kingston HM and Riviello JM (1990) Chelation ion chromatography as a method for trace elemental analysis in complex environmental and biological samples. *Analytical Chemistry* 62: 1185–1193.

Timberbaev AR and Bonn GK (1993) Complexation in ion chromatography – an overview of developments and trends in metal analysis. *Journal of Chromatography* 640: 195–206.

Weiss J (1995) *Ion Chromatography*, 2nd edn, Weinheim: VCH.

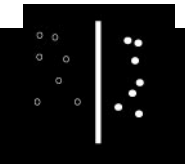
Wilkins DH (1959) The separation and determination of nickel, chromium, cobalt, iron, titanium, tungsten, molybdenum, niobium, and tantalum in a high temperature alloy by anion exchange. *Talanta* 2: 355–360.

DropBooks

Use in Gas Separation

See **III / GAS SEPARATION BY METAL COMPLEXES: MEMBRANE SEPARATIONS**

METAL MEMBRANES: MEMBRANE SEPARATIONS



Y. S. Lin and R. E. Buxbaum, University of Cincinnati, Cincinnati, OH, USA

Copyright © 2000 Academic Press

Introduction

The use of metal membranes for hydrogen separation was first demonstrated over a century ago. Graham discovered in 1866 that palladium absorbs a suprising

amount of hydrogen. Graham went on to show that palladium and palladium–silver membranes permeate only hydrogen, paving the way for the use of metal membranes for hydrogen extraction and purification. Much of the earlier knowledge in metal membranes is summarized in three reference books published in 1967–1968 (see Further Reading). Recent academic research is reviewed in seversl monographs on inorganic membranes and review articles. This article gives an overview of the general properties of metal membranes, followed with a description of methods that have been developed for membrane fabrication. Applications of the metal membranes in separation and chemical reaction processes and design of the metal membrane separation processes are descibed later in the article.

General Properties of Metallic Membranes

A surprising amount of hydrogen can be absorbed reversibly by palladium alloys and by many transition metals over a large temperature range. The absorption proceeds via interstitial incorporation in the metal, generally leaving the crystalline structure intact. Thus, for example, face-centered cubic palladium retains its structure to the metal hydride phase, with the hydrogen progressively occupying tetrahedral and octahedral sites. The nature of the chemical bonding is still not well understood, but a widely used model assumes that the hydride is an alloy (in the usual metallic sense) of hydrogen and the host metal. Electrons from the hydrogen progressively occupy the d-bands of the transition metal, and the hydrogen exists essentially as slightly shielded protons in the host lattice. The other model is based on a predominantly covalent bond between the metal and hydrogen. In this model molecular hydrogen is dissociated to become atomic hydrogen, which subsequently forms chemical-type bonds to the host metal.

Figure 1 shows hydrogen solubility relationships for several transition metals at different temperatures. At constant pressure, the hydrogen solubility of some metals increases with increasing temperature, while for some other metals it decreases. **Figure 2** shows typical relationships of hydrogen solubility (presented in the atomic ratio of hydrogen to metal) versus hydrogen partial pressures at different temperatures. The dashed curve in Figure 2 encloses the two-phase region of the palladium hydride system with α-phase to its left and β-phase to its right. For all metals below their hydride phase transition, the solubility increases with hydrogen pressure. The most common relationship for this is

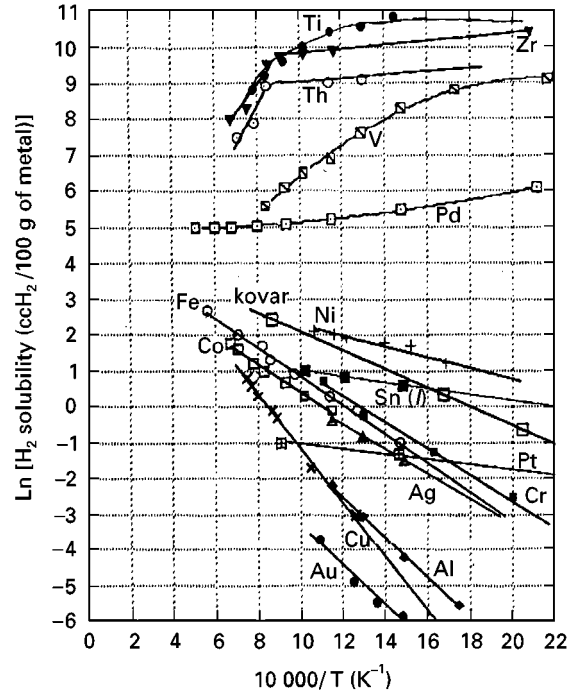


Figure 1 Hydrogen solubility of several transition metals at different temperatures ($P_{H_2} = 1$ atm). (Copyright REB Research & Consulting with permission.)

the Sievert's relation:

$$C = K_s P^{\frac{1}{2}} \qquad [1]$$

That is to say that the hydrogen concentration, expressed as the ratio of hydrogen : metal or as the volume of hydrogen per gram of metal, is proportional to a temperature dependent constant (K_s) times the hydrogen pressure to the power $\frac{1}{2}$. The power $\frac{1}{2}$ in eqn [1] comes from the entropic effect of every molecule of hydrogen dissociating into two hydrogen atoms in the metal.

Aside from solubility, the most important qualities of a metal for use in metallic membranes are the hydrogen diffusivity in metal and the rates of dissociation and recombination reactions on the membrane surfaces. At the upstream membrane surface the surface reaction step consists of adsorption of H_2, dissociation of this adsorbed H_2 into two hydrogen atoms (or charge-transfer reaction to form protons), and absorption of the atoms into the bulk metal. In the bulk there is a net transport of hydrogen atoms from high to low partial pressure sides along the concentraction gradient. At the downstream membrane surface there is another surface reaction step including the formation of hydrogen molecules from hydrogen atoms (or protons) and desorption of hydrogen molecules from the surface to the gas phase.

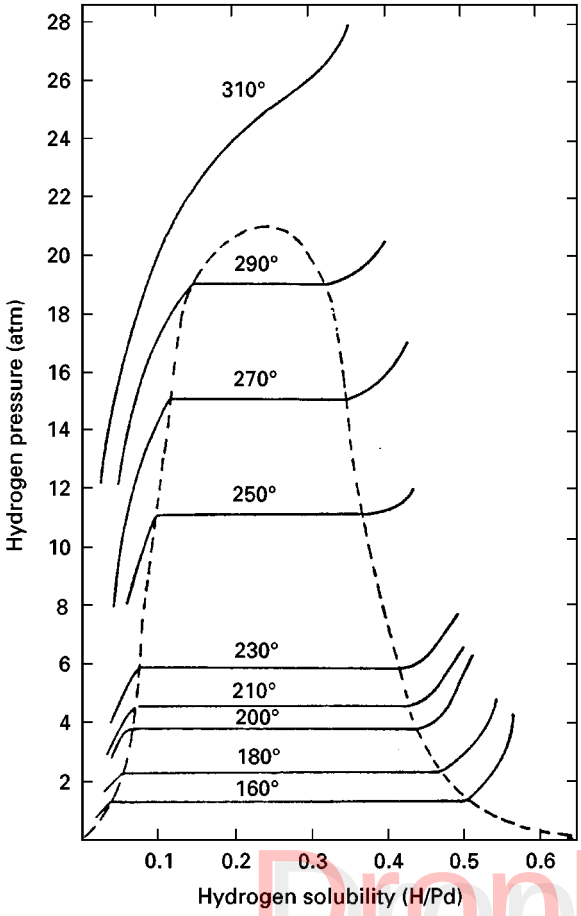


Figure 2 Hydrogen solubility of palladium at different hydrogen pressures and temperatures (°C) (From Lewis FA (1967) *The Palladium Hydrogen System*. Fig. 2.3, p. 17. New York: Academic Press.)

Based on the Mass Action Law, the following simplified equations can be obtained to describe the combined effects on hydrogen permeation flux:

$$J = K_R(P_{UH} - P_I) \quad [2]$$

$$J = (DK_s/2L)\,(P_I^{\frac{1}{2}} - P_{II}^{\frac{1}{2}}) \quad [3]$$

$$J = K_R(P_{II} - P_{DH}) \quad [4]$$

where P_{UH} is the upstream hydrogen pressure, P_{DH} is the downstream hydrogen pressure, P_I is the imaginary pressure in equilibrium with the upstream surface of the metal, and P_{II} is the imaginary presure in equilibrium with the downstream surface. K_R is a lumped rate constant for the surface reaction step. In eqn [3], DK_s is the product diffusivity and Sievert's constant in the bulk metal membrane and L is the membrane thickness. Often $DK_s/2$ is called the hydrogen permeability and is plotted in **Figure 3** for several metals. It should be noted that metal membranes are practically impermeable to other gases such as helium or nitrogen due to their low solubility and diffusivity in the metals. Although for all the metals of interest to separation applications, the hydrogen diffusivity increases and solubility decreases with increasing temperature, we find for some metals (e.g. palladium) the permeability increases with temperature, while for others (e.g. tantalum, niobium) it decreases. The determining factor is the relative temperature dependency of diffusivity and solubility. Because of slow reaction steps (eqn [2] and eqn [4]), permeation membranes of Nb, V and Ta must be coated with palladium to be used for separation applications.

For most metal membranes, bulk diffusion is rate-limiting. That is, $(DK_s/2L)$ is typically smaller than K_R. For such membranes eqn [3] describes the flux with P_{II} and P_I replaced by P_{UH} and P_{DH}. In this case, the hydrogen permeance is inversely proportional to the membrane thickness with permeation flux exhibiting a $P_{H_2}^{\frac{1}{2}}$ dependence. This relationship is referred to as the Richardson's law. If the surface steps are rate-limiting, i.e. $(DK_s/2L)$ much larger than K_R, the hydrogen permeation flux is proportional to the transmembrane pressure drop. When resistances of both surface and bulk steps are equally important, the above equations are sometimes approximated with $P_{H_2}^{0.7}$ dependencies or similar simplified relations.

DropBooks

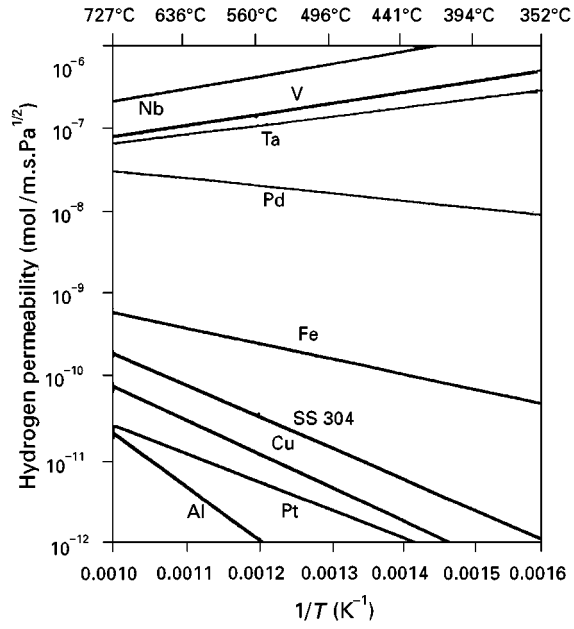


Figure 3 Hydrogen permeability of various transition metals at different temperatures. (Copyright REB Research & Consulting with permission.)

Another critical behaviour for any metallic membrane is durability. Figure 2 shows that below a critical temperature (310°C) palladium hydride can exist either in the α-phase or β-phase, depending on hydrogen pressure and temperature. Above the critical temperature, palladium hydride remains in the α-phase regardless of the hydrogen partial pressure. Both the α-phase and β-phase have the same face-centered cubic lattice structure, but the lattice constant of the latter is as much as 3% larger than the former. Thus, a hydrogen pressure swing below the critical temperature or a temperature swing (above the critical pressure) will cause large mechanical strains during phase transformation of the palladium hydride between the two phases. These lattice strains would destroy the mechanical integrity of a membrane made of palladium alone. This phenomenon is referred to as 'hydrogen embrittlement'. For practical application this is avoided by alloying the palladium and by lowering the hydrogen pressure sharply before the membrane cools to room temperature. The same problems and solutions are also applicable to Pd-coated transition metals.

Alloying palladium with silver results in a phase diagram with a decreased critical temperature and pressure. If we accept the metallic alloy model for metal–hydride systems, the role of silver can be explained as an electron-donating behaviour where electrons from silver and hydrogen atoms compete for filling the 4d-band of palladium. Since 4d-band filling is associated with β-phase formation, 40% silver prevents β-phase formation entirely although most common alloys do not employ quite so much silver. Once the 4d-band is filled, electrons from further hydrogen absorption contributes to 5s-band filling and the net effect is decrease in both critical temperature and pressure in the phase diagram. Common palladium–silver (23–25% silver) membranes and palladium–copper membranes can be operated at much lower temperatures than pure palladium membranes without significant hydrogen-embrittlement problems. This is especially true if care is taken at start-up and shutdown to avoid exposure of the membranes to high-pressure hydrogen at room temperature.

Metal membranes are susceptible to surface poisoning. Prolonged exposure of many metal membranes to sulfur or even carbon containing gases under some conditions could deactivate the membrane surface or change the bulk structure of thin metal membrane, affecting adversely the membrane permeation and separation properties. The current approach is to avoid this problem by removing poisoning impurities from the gas stream prior to the contact with the membrane surface. Modification of the metal surface to improve its resistance to surface poisoning may provide an inherent solution to this problem. Research efforts in finding a suitable modification method have been limited, but are expected to increase in the future.

Fabrication of Metal Membranes

Casting/rolling is the current method for commercial production of palladium-based metal membranes. This method involves several steps. Membrane raw materials are melted at a high temperature to form ingots which go subsequently through hot or cold forging or pressing to produce tube or sheet. The final membrane has a thickness typically in the range of 50 to 75 μm (0.002–0.003 in). The metal membranes prepared by this method are polycrystalline with large grains (submicron or micron size). Furthermore, cold rolling often generates lattice dislocation and it can enhance hydrogen solubility in palladium and some of its alloys due to the accumulation of hydrogen around the dislocation. As a result, these polycrystalline metal membranes have very high hydrogen solubility.

Based on the Richardson equation (eqn [3]), thin metal membranes are more desired than thick ones in terms of hydrogen permeance and metal cost savings. The problem has been in forming such membranes and keeping them stable during temperature and pressure cycling. To improve the durability, thin metal membranes have been formed by coating on porous metallic or ceramic support. Several methods have emerged in the past decade for this including liquid-phase electroless plating and chemical vapour deposition (CVD).

Electroless plating involves autocatalysed decomposition of a selected metastable metal presursor such as $Pd(NH_3)_4X_2$ where X can be NO_3, Cl or Br in alkaline aqueous solution at around 50°C. To avoid autodecomposition of the metal precursors a stabilizer such as ethylenediaminetetraacetic acid (EDTA) is often added. For nonmetallic supports, the surface (substrate) should be activated, e.g. by $SnCl_2$/PdCl, prior to electroless plating. Palladium or palladium–silver films with a thickness ranging from 5 to 30 μm have been prepared by this method on supports of porous alumina and stainless steel and on non-porous niobium, tantalum or vanadium alloy.

Thin metal membranes can also be prepared by CVD of metal salts and metal organic compounds, such as $PdCl_2$ and $Pd(O_2C_5H_7)_2$ and can also be produced by sputter coating of a solid metal. For CVD, the precursor vapour, with or without a reducing agent (hydrogen), is brought in contact with one surface of the porous support at a high temperature.

Reduction of the precursor occurs directly or by countercurrent exposure to the reducing agent at 200–400 °C. Palladium films as thin as 0.5 μm have been deposited on or inside porous alumina support this way. For sputter deposition a metal target of desired composition is placed apart from the substrate in a sputtering chamber filled with a working gas (argon) at low pressure (about 10^{-3} torr). A DC or radiofrequency AC electric-field gradient plasma is generated in the working gas and bombards the target. Fine metal particles or atoms dislodged from the target move towards the substrate and subsequently deposit. Thin palladium and palladium–silver membranes have been coated on porous γ-alumina and dense polymer substrates by this method.

Metal membranes prepared by the vapour methods are usually nanocrystalline with grain size in the range of a few tens of nanometers. Electroless-plated metal membranes appear to be more coarse-grained. For palladium on substrate membranes, the bulk diffusion step in the substrate is generally the rate-limiting step. Furthermore, fine-grained thin metal membranes appear to have a lower hydrogen permeability than coarse-grained thick metal membranes. Thus, while the metal cost for Pd-coated ceramics is typically much lower than for symmetric metal membranes, the flux is usually fairly similar and can even be lower than traditional metal membranes, and is typically proportional to the pressure dependence and not to $P_{H_2}^{\frac{1}{2}}$ as in eqn [3]. Similar membrances prepared by different methods can exhibit different dependency, and specific relationships should be obtained in order to design separation and reaction processes involving these metal membranes.

DropBooks

Metal Membrane Applications

The major large-scale application for metal membranes today is hydrogen purification, with most of that hydrogen used for interated circuit manufacture. Different circuit technologies differ in the purity of hydrogen they require, and the current needs are between 5 nines (99.999%) and 8 nines (99.999999%) hydrogen, or 0.01 to 10 ppm impurities. The largest user, silicon-based semiconductor manufacture requires the lower levels of purity, and gallium arsenide the highest. These purity levels are expected to increase over time as transistor densities rise, doubling approximately every two years. Silicon applications should thus need 7 nines and gallium arsenide applications 9 nines hydrogen by 2005.

Metal membrane purification competes with adsorption technology for the market in electronic component manufacturing. The metal membrane market is valued at only $10 millions/year, but the ultrapure hydrogen delivery market is at least 100 times bigger suggesting significant room for growth in purifier sales. For electronic component manufacturing using cylinder hydrogen (the only choice in much of the Far East) there is no real alternative to membrane purification using tubular membranes of palladium–silver alloy (23–25% silver). The leading companies in this market are Johnson Matthey (75% market share) and Japan Pionics (25% market share.) Cylinder hydrogen is so impure that competing getter technology is not cost effective. Competing getter technology is often preferred with liquid hydrogen sources (available in the USA and Europe) because the pressure drop is lower and since the delivered hydrogen is purer, the cost is lower as well. Even here, membranes are often used for high value-added parts since getters tend to release small amounts of oxide dust as they saturate with impurities. This oxide can interfere with semiconductors manufacture and presents a safety hazard, e.g. released vanadium oxide dust is highly toxic with an exposure limit of 0.05 mg m^{-3}. Membranes are also safety favourites since the main getter alloys are flammable in contact with air at operating temperatures as high as 600°C.

A second major application for metal membrane purified hydrogen is as a carrier gas for gas chromatography. This is true particularly in Europe and the Far East where helium is scarce, but also in the USA for fast-response, high-sensitivity applications. The purity need here could be met by ultrapure cylinders, especially backed by a getter trap, but it is cost effective to use a membrane. An 'A-size' cylinder, containing 65 ft^3 (STP) (1900 L (STP)) of ultrapure zero-grade hydrogen costs approximately $220 currently. Continuous use as a carrier and reference gas consumes about 150 cm^3 (STP) min^{-1}, emptying the cylinder in slightly over a week, and costing the customer $10 000 annually. A membrane purifier of very modest size will allow the customer to use a much cheaper, lower grade of hydrogen, returning the purchase cost in six months or less.

Palladium membranes are also used for isotope enrichment providing a separation factor of about 1.4 for protium over deuterium, and about 1.7 for protium over tritium. While the hydrogen volume need for this application is small, the low separation factor ensures that quite a lot of membrane is needed.

A rather new line of metal membrane applications is for membrane reactors, mainly to generate hydrogen for fuel cells, but also to promote thermodynamically unfavourable reactions like methane splitting and ethylene production. A membrane reactor combines, in one unit, a catalytic reactor bed and a membrane separator to remove a desired

product (hydrogen) as it is formed. As a result membrane reactors drive the reaction towards completion and achieve advantages of enhanced catalyst use, higher feed space velocity and fewer side products.

Another benefit of membrane reactors, particularly for fuel cell applications that require high-purity hydrogen from source gases like methanol or gasoline, is that a membrane changes the way pressure affects extent of reaction and product recovery. Without the membrane in the reactor, a reforming reaction of this type would require low pressure operation to achieve high conversion, and would require a difficult hydrogen purification for the intended use. A membrane reactor allows the reaction to be driven by high pressures, greatly increasing the ease of hydrogen product recovery. At present, several membrane reactors are in trial and one at the pilot-plant scale for the production of hydrogen. Typical pressures of operation are at 17 atm, with operation temperatures dictated by the catalyst and material of construction. The size of the fuel cell market is currently small, but is believed to be rising fast.

Designs of Metal Membrane Separation Processes

Figure 4 shows the basic design of a hydrogen purifier. Prominently shown is a heat exchanger set between the input hydrogen feed and the purified hydrogen product. Heat recovery of this type is critical because the membranes typically operate at 350–400°C in an environment where the source gas and product application are near room temperature. Heat exchange cools the output gas and reduces the electric heating costs. Heat exchange also promotes temperature uniformity within the purifier; this is an important consideration since for most of the hydrogen permeable alloys a 100°C temperature gradient in the membrane would mean that part of the membrane would have to operate at significantly below their optimal temperature for flux, and part of the membrane would operate at significantly above the optimal temperature for long life.

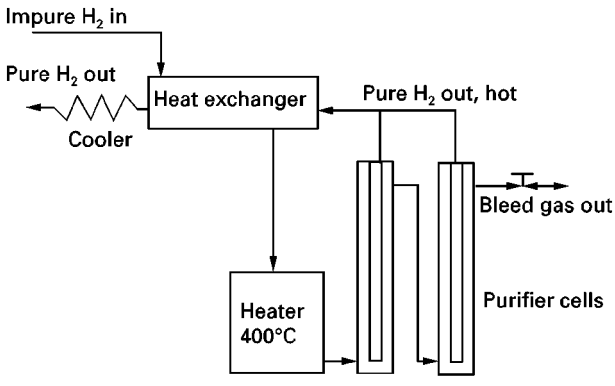


Figure 4 Schematic diagram of a metal membrane hydrogen purifier process. (Courtesy of Johnson Matthey, plc.)

Figure 4 also shows a bleed valve to control the removal of impurities from the purifier, and a system to provide inert gas (nitogen) flushing. Setting these systems is something of an art, since with too little bleed, impurities would build up in the purifier reducing the hydrogen output. Too much bleed, by contrast, results in a loss of heat and pressure resulting in a similar reduction in output. Most larger purifiers provide a nitrogen purge system as shown, to help extend the life of the membrane by reducing hydrogen embrittlement of the palladium alloys. This purge system can also be a source of problems as purging can result in hydrogen being sucked back into the purifier. If the sucked back hydrogen is contaminated with other electronic gases (particularly arsine) this will result in an irreversibly poisoned membrane.

There are basically two types of tubular membrane based commercial purifier designs: pressure-outside and pressure-inside. Until recently, large-scale hydrogen purification (>100 L (STP) min^{-1}) was limited to pressure-outside design. **Figure 5** shows schematic of a pressure-outside design. The inlet flow of fluid containing a mixed gas includes hydrogen flows over the outer surface of the metal membrane tubes housed inside a pressure vessel. The metal membrane tubes are operatively connected at one end to a header and the other end of the tubes are either capped or can be operatively attached to a floating head. Hydrogen permeates from outside into the inside of the metal membrane tubes, and leaves the membrane module through the outlet port. Pressure-outside designs (Johnson Matthey, Japan Pionics, and REB Research & Consulting) have longer life than the pressure-inside designs since the former do not require a braze seal at both ends of the membrane tube.

Pressure-inside designs, supplied by REB Research & Consulting, RSI and Power & Energy, are believed to output somewhat purer hydrogen because the impure gas flow past the membrane is more uniform than with pressure-outside designs. In the pressure-inside designs, the pressure drop and vibration effects in the tubes become excessive as tube lengths exceed 25–50 in. (63–127 cm). These effects could be effectively minimized by a scheme for placing several short lengths of Pd–Ag or similar tube in parallel while balancing the flow through each using matched, internally located flow restrictors. Forces of expansion and contraction by the membranes against the seals are believed to be a major

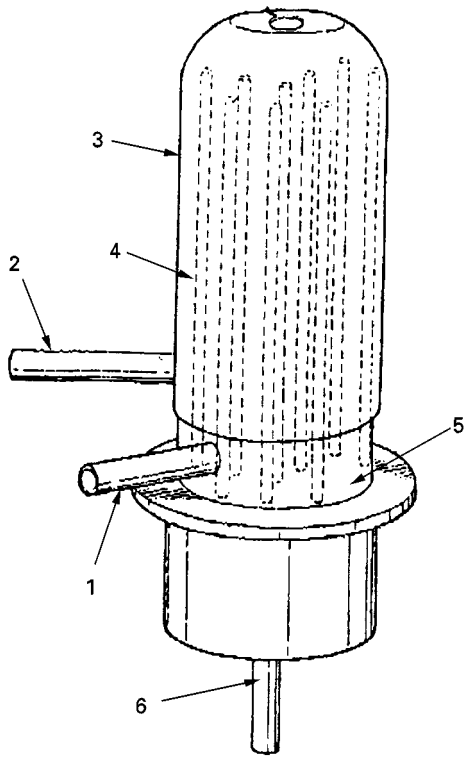


Figure 5 Schematic diagram of a pressure-outside design of metal membrane module: 1. Feed gas inlet. 2. Feed gas outlet. 3. Pressure vessel. 4. Metal membrane tubes. 5. Header. 6. Pure hydrogen outlet. (From US Patent 5,931,987, 1999.)

cause of fatigue failure in pressure-inside designs, as is burnthrough. Burnthrough is believed to be a bigger problem with pressure-inside designs since metals are inherently more stable in compression than in tension. That is a tube in compression will flow somewhat to heal a thin spot, but will flow away in tension turning a thin spot into a hole.

A third type of purifier using flat plates of Pd–Cu was recently demonstrated by Northwest Power. As flat plates can be made thinner than metal tubes the output flux with these membrane is exceptional. Unfortunately welded seals are much less reliable in this configuration than with tubes and instead graphite seals are used. The degree of purification from these devices is unacceptable for integrated circuit manufacture, but appears to be acceptable for use with fuel cells.

Almost all commercial metal membrane separation systems use the symmetric solid metal membranes fabricated by the conventional casting/rolling method. The only commercial attempt at using porous substrate supported metal membranes was in the 1950s and 1960s by Union Carbide who applied a thin layer of palladium–silver alloy on a porous ceramic substrate. By choosing the pore size and thickness appropriately, metal cost per unit area could be decreased significantly while flux could be increased somewhat. The early membranes did not prove durable though, and had to be removed from service. Results with all of these alternatives is encouraging but it is fair to say that the commercial metal membrane market is still dominated by unsupported palladium alloys. The main reason is purity and durability: both the Pd-coated refractory metals and the Pd coated porous substrates have shown less cycling durability than typically associated with the solid Pd alloys, and the purity of hydrogen purified through the newer membranes has still to reach the very high levels of solid membrane purifiers. This latter is particularly significant for the high value added applications that dominate the metal membrane market currently.

Concluding Remarks

Metal membranes are the most hydrogen perm-selective inorganic membranes in the temperature range of 200–500°C. They are expected to remain so in the near future. Much progress has been made in understanding metal membrane properties and development of various methods for metal membrane fabrications. However, applications of metal membranes have been limited to hydrogen purification. In addition to the structural stability and cost problems, another major problem for metal membranes is their susceptibility to surface poisoning. This problem has to be solved in order for the metal membranes to gain wider acceptance in processes for separation of hydrogen containing gases of industrial importance.

DropBooks

Further Reading

Armor JN (1998) Applications of catalytic inorganic membrane reactors to refinery products. *Journal of Membrane Science* 147: 217–233.

Bhave RR (1991) *Inorganic Membranes. Synthesis, Characteristics and Applications*. New York: van Nostrand Reinhold.

Burggraf AJ and Cot L (eds) (1995) *Fundamentals of Inorganic Membrane Science and Technology*. Amsterdam: Elsevier.

Buxbaum RE (1999) Membrane reactor advantages for methanol reforming and similar reactions. *Separation Science and Technology* 34: 2113–2123.

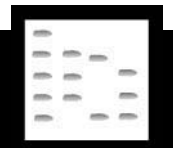
Buxbaum RE (1999) US Patent 5,888,273. *High Temperature Gas Purification System*. March 30.

Buxbaum RE and Kinney AB (1996) Hydrogen transport through tubular membranes of palladium-coated tantalum and niobium. *I&EC Research* 35: 530–537.

Hsieh HP (1996) *Inorganic Membranes for Separation and Reaction*. Amsterdam: Elsevier.

Hwang ST and Kammermeyer K (1984) *Membranes in Separation*. Malabar, Florida: Rorbert E. Krieger.
Lewis FA (1967) *The Palladium Hydrogen System*. London: Academic Press.
Mueller WM, Blackledge JP and Libowitz GG (1968) *Metal Hydrides*. New York: Academic Press.
Shu J, Grandjean BPA, Van Neste, A and Kaliaguine S (1991) Catalytic palladium-based membrane reactors. A review. *Canadian Journal of Chemical Engineering* 69: 1036–1060.
Uemiya U (1999) State-of-the-art of supported metal membranes for gas separation. *Separation and Purification Methods* 28: 51–85.
Wise EM (1968) *Palladium Recovery, Properties and Uses*. London: Academic Press.

METAL UPTAKE ON MICROORGANISMS AND BIOMATERIALS: ION EXCHANGE



H. Eccles, British Nuclear Fuels, Preston, UK

Copyright © 2000 Academic Press

Introduction

Microorganisms and biomaterials can be used for the removal/recovery of metals from process liquors and liquid wastes. The mechanisms involved in capturing metals from solution by microorganisms and related materials are now commonly referred to as biosorption. Biosorption has been defined as the removal of metals or metalloid species, compounds and particulates from solution by biological material. It is one of the fields in environmental biotechnology, which is itself a small, but growing, component of the biotechnology industry (**Figure 1**).

The use of microorganisms to treat waste liquors on a commercial scale dates back to the end of the nineteenth century when the first communal sewage plants in Berlin, Hamburg, Munich, Paris and other major cities came into operation. In the intervening 100 years the use of microorganisms and plants to protect the environment has developed into a multi-billion dollar (US$) industry. However, the foundations of this environmental biotechnology industry are still with the treatment of municipal/domestic effluents.

Although nature has demonstrated some subtle and intricate mechanisms for selectively controlling the mobility of pollutants in the environment, the conversion of this science to technology and to application has been very disappointing. In explaining this lack of application, it is important that these mechanisms

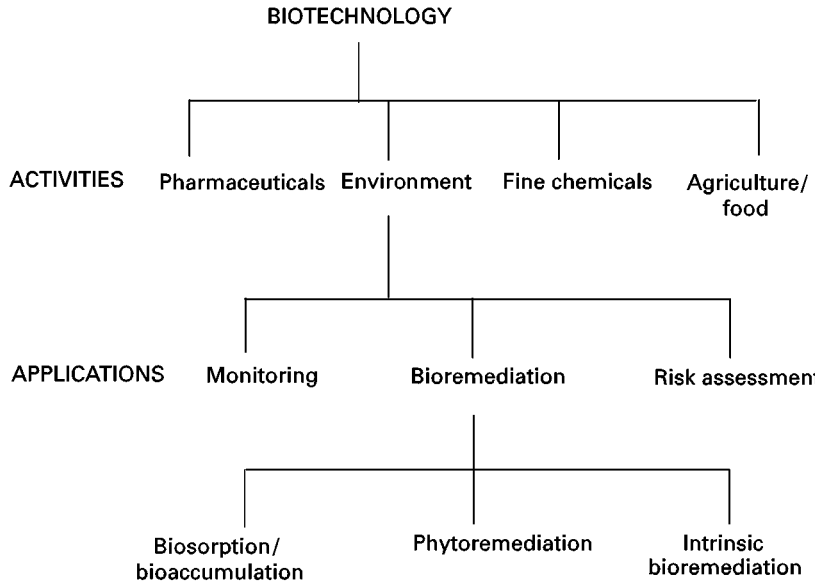


Figure 1 Biotechnology activities and applications. (This is an original developed by H Eccles.)